

RESEARCH ARTICLE

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Key Points:

- Poulsen et al. (2015) suggested that warm Cenomanian surface temperatures were caused by low oxygen
- We use a 1-D radiative-convective model to assess the results of Poulsen et al. (2015)
- Our results oppose theirs, with the warmest surface temperatures occurring with high oxygen

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The response of Phanerozoic surface temperature to variations in atmospheric oxygen concentration

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Abstract Recently, Poulsen et al. (2015) suggested that O₂ has played a major role in climate forcing during the Phanerozoic. Specifically, they argued that decreased O₂ levels during the Cenomanian stage of the middle Cretaceous (94–100 Ma) could help explain the extremely warm climate during that time. The postulated warming mechanism involves decreased Rayleigh scattering by a thinner atmosphere, which reduces the planetary albedo and allows greater surface warming. This warming effect is then amplified by cloud feedbacks within their 3-D climate model. This increase in shortwave surface forcing, in their calculations, exceeds any decrease in the greenhouse effect caused by decreased O₂. Here we use a 1-D radiative-convective climate model (with no cloud feedback) to check their results. We also include a self-consistent calculation of the change in atmospheric ozone and its effect on climate. Our results are opposite to those of Poulsen et al.: we find that the climate warms by 1.4 K at 35% O₂ concentrations as a result of increased pressure broadening of CO₂ and H₂O absorption lines and cools by 0.8 K at 10% O₂ as a result of decreased pressure broadening. The surface temperature changes are only about 1 K either way, though, for reasonable variations in Phanerozoic O₂ concentrations (10%–35% by volume). Hence, it seems unlikely that changes in atmospheric O₂ account for the warm climate of the Cenomanian. Other factors, such as a higher-than-expected sensitivity of climate to increased CO₂ concentrations, may be required to obtain agreement with the paleoclimate data.

1. Introduction

Poulsen et al. [2015] have recently argued that changing atmospheric O₂ concentrations may have been an important driver of climate during the Phanerozoic, along with changing atmospheric CO₂. They used the Global Environmental and Ecological Simulation of Interactive Systems (GENESIS) 3-D climate model to simulate a baseline middle-Cretaceous climate with 21% O₂, along with 1120 ppmv CO₂, and a solar constant of 0.9943 times the present value. They then looked at the effect of varying the atmospheric O₂ mixing ratio from 10% to 35%, which corresponds to the lower and upper bounds derived from a charcoal O₂ proxy [Scott and Glasspool, 2006]. They found that the global mean temperature increased by 2.1 K for the low-O₂ calculation and decreased by 2.3 K for the high-O₂ calculation. The suggested mechanism was decreased Rayleigh scattering at low O₂ levels, leading to a decrease in reflected solar radiation and a corresponding rise in surface temperature. At higher O₂ levels, increased Rayleigh scattering lowered the surface temperature in their model. Cloud feedbacks were also argued to be important in determining the climate response to O₂ forcing.

To test whether these results are robust, we used a version of our own 1-D climate model [Segura et al., 2003] to perform a similar calculation. The 2003 model version was used with the RRTM (Rapid Radiative Transfer Model) of Mlawer et al. [1997] for infrared radiation because this model has been well vetted for present Earth conditions. Instead of simulating the middle Cretaceous, as Poulsen et al. did, we computed the effects of changing O₂ in the modern atmosphere. In our model, these effects are nearly identical to those obtained for middle-Cretaceous conditions. We also used a 1-D photochemical model to compute self-consistent ozone changes for these changes in O₂, as well as related trace gases such as CH₄ and N₂O, and we calculated the accompanying changes in surface temperature caused by the ozone changes.

2. Conservation of Nitrogen

Before describing our calculations, we first point out that one must be careful when adding or subtracting O₂ from a model atmosphere because the partial pressure of a gas is not linearly related to its column

abundance when the surface pressure changes. Poulsen *et al.* [2015] calculated the change in atmospheric pressure caused by adding or removing O₂ by adding/subtracting partial pressures. It can be shown that this methodology does not conserve the column mass of other atmospheric constituents, in this case N₂ and Ar. The reason is that, in seeming contradiction with Dalton's Law, the partial pressure of one atmospheric gas does depend on the partial pressures of the other gases in a column of air under the influence of gravity. Adding a lighter gas to a heavier one increases the atmospheric scale height and causes the heavier gas to spread vertically, decreasing its partial pressure at the surface. The errors introduced by incorrectly changing the atmospheric pressure are modest (about 2%) when expressed in terms of total atmospheric pressure. However, if one calculates the error relative to the change in atmospheric pressure expected at 10% O₂ or 35% O₂, the error is much higher, at roughly 10%.

Below, we outline a method for changing the O₂ volume mixing ratio while conserving the column masses of N₂ and Ar. For simplicity, we adopt modern volume mixing ratios of the modern Earth scenario, with values, C_i , of 0.21 for O₂, 0.78 for N₂, and 0.01 for Ar. To begin, we conserve the current ratio of N₂ to Ar, $R_{N_2Ar} = 1/78$. We also need to initialize the atmospheric column mass, which is given by

$$M_{col}^a = \frac{P_s}{g} \quad (1)$$

Here P_s is surface pressure and g is gravitational acceleration. We next compute the mean molecular mass as

$$m = (C_{O_2} \cdot 32 + C_{N_2} \cdot 28 + C_{Ar} \cdot 40) \cdot m_H \quad (2)$$

where m_H is the mass of a hydrogen atom. The column mass of each individual species, i , is then computed from

$$M_{col}^i = C_i M_{col}^a \left(\frac{m_i}{m} \right) \quad (3)$$

where m_i is the species molecular mass. We then get the column number density of each gas by dividing its column mass density by its molecular mass

$$N_{col}^i = \frac{M_{col}^i}{m_i} \quad (4)$$

When we change the O₂ mixing ratio, we must recalculate the mixing ratio of N₂ and Ar. These mixing ratios must sum to unity, such that

$$C_{O_2}' + C_{N_2}' + C_{Ar}' = C_{O_2}' + C_{N_2}'(1 + R_{N_2Ar}) = 1 \quad (5)$$

So,

$$C_{N_2}' = \frac{1 - C_{O_2}'}{1 + R_{N_2Ar}} \quad (6)$$

$$C_{Ar}' = C_{N_2}' R_{N_2Ar} \quad (7)$$

We use these new mixing ratios to compute a new mean molecular mass from equation (2).

The rest of the procedure requires iterations, as the total column changes. First, we calculate a new column number density of O₂ from $N_{col}^{O_2} = C_{O_2}' N_{col}^a$, where N_{col}^a is the total column number density. Then, add this to $N_{col}^{N_2} + N_{col}^{Ar}$ to get a new value for N_{col}^a . Now recalculate $N_{col}^{O_2}$ using the new value of N_{col}^a . N_{col}^a changes in each iteration. Using the new $N_{col}^{O_2}$, we can convert it back to column mass using $M_{col}^{O_2} = \frac{N_{col}^{O_2}}{32 m_H}$. Add this value to the column masses of N₂ and Ar (which were held constant) to compute a new total column mass, M_{col}^a . Finally, from this, we find the new surface pressure P_s using equation (1).

To ascertain that we have indeed conserved nitrogen with an altered C_{O_2} value, we check the final column mass of nitrogen after the final iteration using equation (3), which is equal to the initial $M_{col}^{N_2}$ at 7787.43 kg/m². These numerical results are summarized in Table 2. Overall, we find a mean 1.6% discrepancy between our calculated surface pressure values and those of Poulsen *et al.* [2015].

Finally, following the methodology of Poulsen *et al.*, we conserve column masses of CH₄ and N₂O by increasing their surface mixing ratios for low O₂ and decreasing them at higher O₂ (see Table 1). Their mixing ratios

Table 1. Effect of Changing O₂ on Surface Volume Mixing Ratios of CH₄ and N₂O With Constant Column Mass or Fixed Upward Flux

| Species | 21% O ₂ | Volume Mixing Ratio | | | |
|------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| | | Constant Column Mass | | Fixed Upward Flux | |
| | | 10% O ₂ | 35% O ₂ | 10% O ₂ | 35% O ₂ |
| CH ₄ | 1.60×10^{-6} | 1.85×10^{-6} | 1.29×10^{-6} | 1.91×10^{-6} | 1.43×10^{-6} |
| N ₂ O | 3.00×10^{-7} | 3.47×10^{-7} | 2.42×10^{-7} | 2.31×10^{-7} | 3.42×10^{-7} |

are inversely proportional to surface pressure. This does not account for changes in their atmospheric photochemistry as O₂ changes, so we also performed a sensitivity study to determine how important these assumptions about CH₄ and N₂O might be. An alternative methodology that of Poulsen *et al.* is to hold the upward fluxes of these gases constant and allow their surface mixing ratios to change freely in response to increasing or decreasing O₂. When this approach is taken, CH₄ continues to vary inversely with surface pressure, but the N₂O mixing ratio increases as O₂ increases and decreases when O₂ decreases (Table 1, last two columns). The reason for this is that higher atmospheric O₂ shields N₂O from photolysis and thus lengthens its atmospheric lifetime. This has a negligible effect on surface temperature; as O₂ is increased from 21% to 35%, surface temperature rises from 289.54 K to 290.86 K with constant upward flux, as opposed to 290.95 K with constant mixing ratios, so the effect of properly scaling N₂O is only on the order of approximately 0.1 K).

3. Radiative Forcing Calculations

Using this methodology, we computed surface pressures for two different O₂ volume mixing ratios, 0.1 and 0.35. We then did three sets of calculations using the Segura *et al.* [2003] radiative-convective climate model. First, we did a control simulation with C_{O₂} = 0.21 and P_s = 101.3 kPa. Results are shown in the second row of Table 2. \bar{M} is the mean molecular weight, T_s (equal to 288.3 K) is the calculated mean surface temperature, A_p is the planetary or top-of-atmosphere (TOA) albedo, F_{IR}^{up} is the outgoing TOA infrared flux, F_{SOL}^{up} is the reflected TOA solar flux, and F_{SOL}^{dn} is the downward solar flux at the surface. Because these are converged simulations, the net TOA flux (net IR minus net solar) is close to zero.

Next, we did two one-step calculations with C_{O₂} changed to 0.1 and 0.35. The goal was to calculate the instantaneous radiative forcing caused by the O₂ change (although doing so requires making several assumptions, as described below). These simulations should indicate the direction and size of the change in greenhouse effect compared to Rayleigh scattering. In these calculations, the vertical temperature profile was kept the same as in the control run, and the model was either stretched or compressed so as to reach the surface. Each model atmosphere has 100 vertical layers, which are unevenly spaced in log pressure. The lowest level is at the surface, so as the surface pressure changes, the pressure at each level also changes. To maintain a self-consistent atmospheric profile, with a convective troposphere, we first reduced the temperatures below the atmospheric cold trap to the cold trap value. However, the surface temperature, T_s, was kept at the control value of 288.3 K. We then drew moist adiabats up from the surface until they intersected with the temperature profile. Finally, we recomputed the water vapor mixing ratio at each pressure level from its saturation vapor pressure and the specified distribution of relative humidity (following Manabe and Wetherald [1967]) and then computed radiative fluxes.

Table 2. Effect of Changing O₂ on Radiative Fluxes for One-Step and Converged Simulations

| O ₂ % | P _s (kPa) | \bar{M} (g/mol) | T _s (K) | A _p | TOA F _{IR} ^{up} (W/m ²) | TOA F _{SOL} ^{up} (W/m ²) | Surf F _{SOL} ^{dn} (W/m ²) | TOA F _{tot} (W/m ²) |
|---|----------------------|-------------------|--------------------|----------------|---|--|---|--|
| <i>Uncoupled One-Step Runs With Unchanged O₃</i> | | | | | | | | |
| 10% | 87.61 | 28.52 | 287.90 | 0.2427 | 260.880 | 82.509 | 255.58 | −3.3895 |
| 21% | 101.3 | 28.96 | 288.27 | 0.2429 | 257.400 | 82.552 | 250.53 | +0.0450 |
| 35% | 125.4 | 29.52 | 288.95 | 0.2440 | 251.100 | 82.973 | 241.37 | +5.9221 |
| <i>Converged Runs With O₃ Change</i> | | | | | | | | |
| 10% | 87.61 | 28.52 | 288.74 | 0.2390 | 258.730 | 81.274 | 252.12 | |
| 21% | 101.3 | 28.96 | 289.54 | 0.2405 | 258.230 | 81.768 | 248.22 | |
| 35% | 125.4 | 29.52 | 290.95 | 0.2431 | 257.350 | 82.651 | 241.72 | |

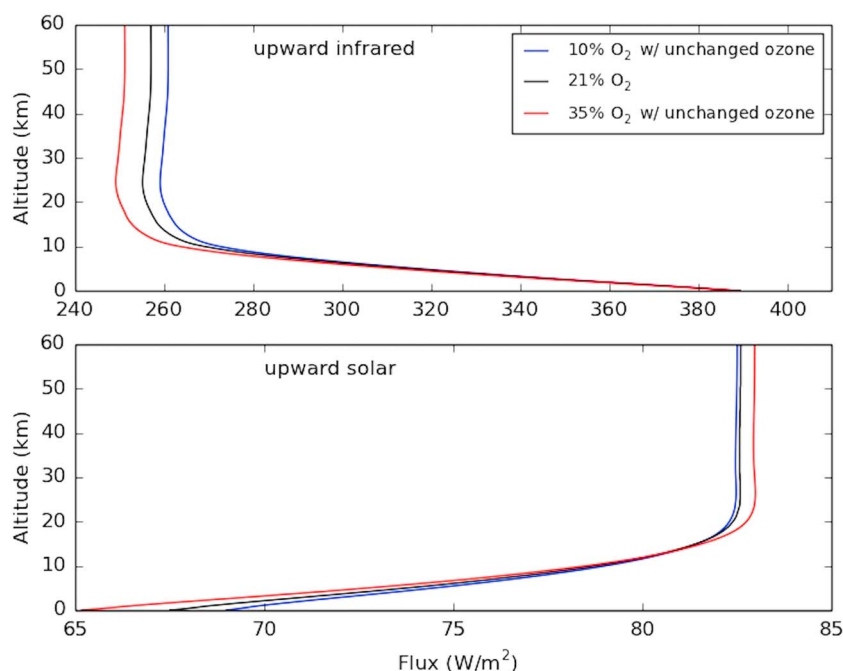


Figure 1. Plot of flux as a function of altitude for the one-step simulations, with O_2 levels of 10% (blue), 21% (black), and 35% (red).

Results are shown in Table 2 and Figure 1. The outgoing solar radiation decreases by about 0.05 W/m^2 in the low- O_2 case and increases by just over 0.4 W/m^2 in the high- O_2 case. These changes are caused by changes in Rayleigh scattering, which decreases with low O_2 and increases with high O_2 as discussed by Poulsen et al. But the outgoing infrared flux changes by a considerably greater amount: it is 3.87 W/m^2 higher in the low- O_2 case and 5.91 W/m^2 lower in the high- O_2 case relative to the control case. These changes in the outgoing IR flux are the result of increased and decreased pressure broadening of absorption lines of CO_2 and H_2O at high- and low- O_2 levels, respectively. In other words, there is more greenhouse warming at higher surface pressure and less greenhouse warming at lower surface pressure, as expected [Strong and Plass, 1950; Goldblatt et al., 2009]. In our model, the change in the greenhouse effect caused by changing O_2 is greater than the change in planetary albedo, so the net radiative forcing is -3.39 W/m^2 at low O_2 and $+5.92 \text{ W/m}^2$ at high O_2 . Our results are similar in sign and general magnitude to independent calculations performed by Goldblatt [2016] using the SMART (Spectral Mapping Atmospheric Radiative Transfer) line-by-line radiative transfer model. Thus, we would predict that our model should warm at higher CO_2 and cool at lower CO_2 , just the opposite of the results of the Poulsen et al. calculations.

The changes in outgoing solar radiation (and associated changes in planetary albedo) for the one-step radiative forcing calculations in Table 2 appear much smaller than those in Poulsen et al. [2015], and it is reasonable to ask why. First, as pointed out by Goldblatt [2016], Poulsen et al. evidently conflated Rayleigh scattering with Mie scattering by cloud particles (see further discussion below). Our model assumes clear skies and so is not subject to such problems. Even so, the effects of Rayleigh scattering on outgoing solar radiation and planetary albedo are quite muted in our model. To see why, we ran additional one-step simulations with the surface albedo set to zero so that the calculated upward solar flux (F_{SOL}^{up}) and planetary albedo would be exclusively caused by Rayleigh scattering (Table 3); by comparison, the surface albedo is set to 0.27 in our standard model, effectively simulating the increased reflection caused by clouds. In these “Rayleigh scattering only” simulations, F_{SOL}^{up} increased by 3.25 W/m^2 as O_2 increased from 21% to 35%, and the planetary albedo increased by 13.73%. So, Rayleigh scattering does make a measureable difference in planetary albedo when the surface albedo is low. For a higher surface albedo, though, or for a more realistic atmosphere in which the planetary albedo is dominated by clouds, Rayleigh scattering is at best a second-order effect.

Although Poulsen et al. did not discuss the effects of pressure broadening, their version of the GENESIS climate model used the radiation code from CCM3 (Kiehl et al. [1998]), which should include this effect.

Table 3. Effect of Changing O₂ on Rayleigh Scattering and the Corresponding Change in Planetary Albedo for Rayleigh Scattering Only One-Step Simulations

| O ₂ % | TOA F_{SOL}^{up} (W/m ²) | A_P From Rayleigh Scattering Only | ΔF_{SOL}^{up} From 21% O ₂ (W/m ²) | ΔA_P From 21% O ₂ |
|------------------|--|-------------------------------------|---|--------------------------------------|
| 10% | 21.575 | 0.0635 | −1.942 | −8.24% |
| 21% | 23.517 | 0.0692 | – | – |
| 35% | 26.768 | 0.0787 | +3.251 | +3.73% |

Indeed, one sees an increase in outgoing longwave radiation in their 10% O₂ case, similar to the increase calculated by our model (see their supporting information Figure 2b). So the difference in results between the two models likely arises from other factors, e.g., the solar radiation code and/or cloud effects.

4. Converged Model Runs

Our one-step radiative forcing calculations described above predict that the climate should warm at high O₂ and cool at low O₂—just the opposite from that found by Poulsen et al. We then tested this prediction by running our own climate model to convergence for the high- and low-O₂ cases. Ozone should also change as O₂ changes, and we wanted to calculate the effect this would have on surface temperature. To do so, we used a 1-D photochemical model from Segura et al. [2003] to calculate ozone profiles for three different O₂ levels: 10%, 21%, and 35%. The CO₂ concentration was held constant at 355 ppmv for these calculations, while the concentrations of CH₄ and N₂O were proportionately increased or decreased (from their present mixing ratios of 1.6 ppmv and 0.3 ppmv, respectively) to keep their column masses constant, as Poulsen et al. did. The O₃ profile was allowed to readjust with changing O₂, and this had a measurable effect on our results.

Next, we coupled the calculated ozone profiles (Figure 3) to the climate model and ran the climate model to convergence. Results are shown in Tables 2 and 4 and Figures 2–4. The 21% O₂ control simulation has a marginally different surface temperature from the one-step calculation, normalized to 289.54 K, because the ozone profile is different from the one used to generate Table 2. Table 4 shows T_s calculated for 10% O₂ and 35% O₂ both with and without the calculated changes in ozone, as well as the difference in T_s from the control simulation.

By comparing the calculations with and without the ozone change included, one can estimate the effect of the changing ozone on surface temperature. Somewhat surprisingly, including the ozone change reduces ΔT_s by a few tenths of a degree in both the 10% and 35% O₂ cases (Figure 4). This may be because the unchanged ozone simulations are actually unphysical, as the ozone layer has been either stretched or shrunk along with the log-pressure grid and is therefore no longer really the same as in the control run. The Poulsen et al. results could be similarly influenced by ozone. They used a prescribed seasonally and latitudinally varying modern ozone profile in all of their simulations, but their vertical grid should also change as the surface pressure changes.

We concentrate, then, on the two simulations in which ozone is modeled self-consistently. In this case, when O₂ is lowered to 10%, T_s decreases by 0.8 K. When O₂ is raised to 35%, T_s increases by 1.4 K. The changes are a factor of 2 smaller and in the opposite direction from those calculated by Poulsen et al. (the Poulsen model cooled by 2.3 K in the high-O₂ case and warmed by 2.2 K in the low-O₂ case). We conclude that changes in the Rayleigh scattering optical depth—identified by Poulsen et al. as the main driver of O₂-forced climate change—are likely not as important as those authors thought. Poulsen et al. combine Rayleigh and Mie scattering in

Table 4. Effect of the Changing O₂ on Various Surface Parameters for Converged Runs With and Without Variable O₃

| O ₂ % | T_s (K) | ΔT_s (K) From 21% O ₂ Control | A_P | F_{SOL}^{dn} (Surface) | O ₃ Column Depth (Molecules/cm ²) |
|-------------------------------|-----------|--|--------|--------------------------|--|
| 10%, unchanged O ₃ | 288.31 | −1.23 | 0.2399 | 252.91 | 8.5079×10^{18} |
| 10% O ₃ change | 288.74 | −0.80 | 0.2390 | 252.12 | 7.7598×10^{18} |
| 21% (control) | 289.54 | 0.0 | 0.2405 | 248.22 | 8.5079×10^{18} |
| 35%, unchanged O ₃ | 291.43 | +1.89 | 0.2418 | 240.75 | 8.5079×10^{18} |
| 35% O ₃ change | 290.95 | +1.41 | 0.2431 | 241.72 | 9.8491×10^{18} |

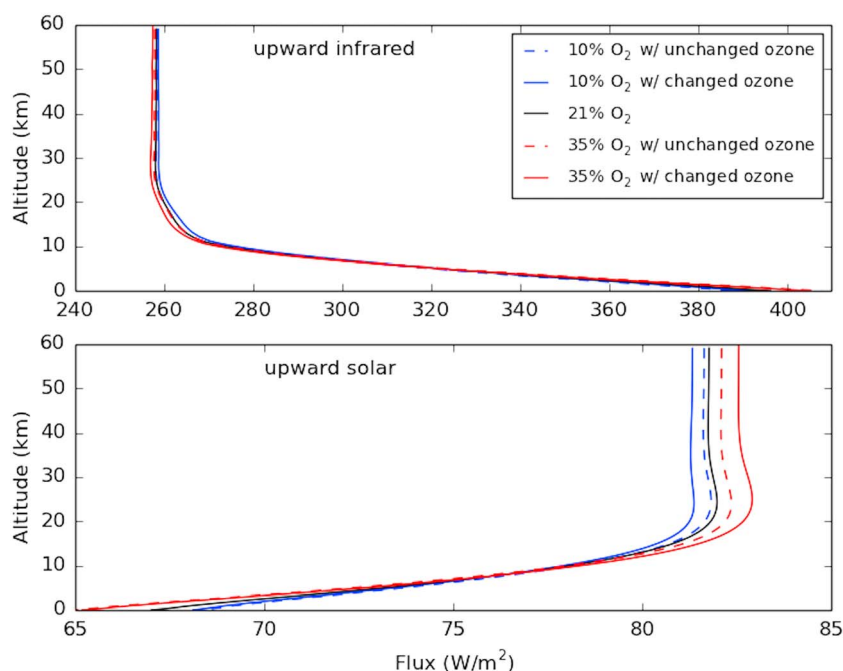


Figure 2. Plot of flux as a function of altitude for the converged simulations. Solid lines indicate simulations with changed ozone profiles according to the concentration of O_2 , while dashed lines indicate simulations with an ozone profile matching that of the control (21%) run (unchanged ozone).

their scaling analysis to result in a decrease in reflected sunlight in low- O_2 conditions. But as Goldblatt [2016] points out in his comment, there is no reason that the number density of cloud droplets should scale with the number density of air molecules, and so the scaling analysis used by Poulsen et al. cannot be justified.

Our own results are consistent with the predictions made earlier based on the instantaneous radiative forcing: when O_2 increases, the change in the greenhouse effect caused by increased pressure broadening outweighs the change in albedo caused by increased Rayleigh scattering; when O_2 decreases, the decreased greenhouse effect has a greater impact on temperature than the decreased Rayleigh scattering. As for Poulsen et al., their results are highly dependent on cloud feedbacks, as they were careful to point out in their paper. Radiative forcing from clouds was 15 to 20 W/m^2 higher in the Poulsen et al. model than in other models,

which would influence any potential cloud-driven warming [Goldblatt, 2016]. Such feedbacks have been ignored in our 1-D climate model, in which the effects of clouds are instead parameterized by adopting a high surface albedo. This does not mean that the Poulsen et al. calculations are necessarily wrong, but it does suggest that their calculations should be checked with an independent 3-D climate model because cloud parameterizations are so uncertain.

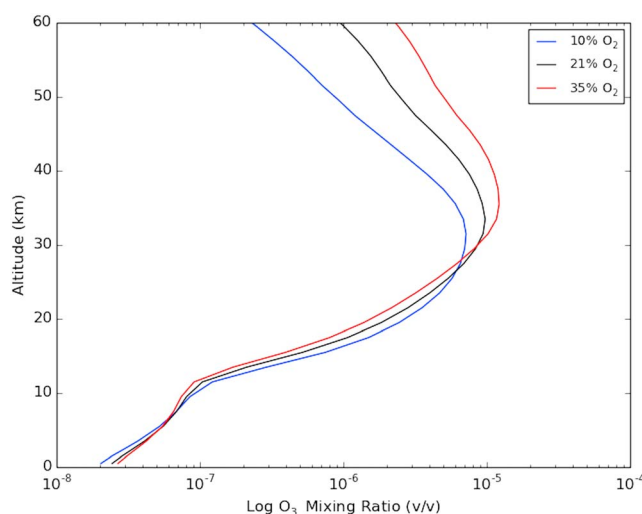


Figure 3. Vertical profile of ozone for the converged simulations.

5. Discussion

We now return to the two observations that motivated the Poulsen et al. calculation. The first is that paleo- CO_2 levels were too low to

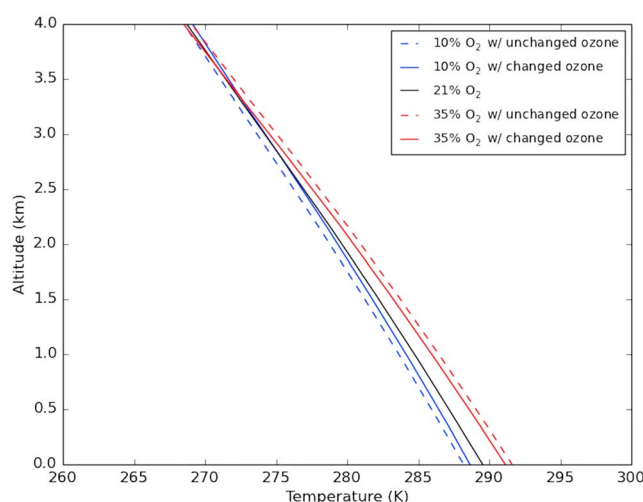


Figure 4. Vertical profile of temperature for the converged simulations.

about 10°C warmer than today, assuming that the poles warmed up to 20°C, as did Cenomanian deep water [Friedrich *et al.*, 2012]. According to Bice *et al.*, attaining these surface temperatures would require at least 4500 ppmv CO₂ in their GENESIS 2.0 3-D climate model. But different climate models have different sensitivities to increases in CO₂. For a middle-of-the-road climate sensitivity of 3° per CO₂ doubling [Intergovernmental Panel on Climate Change, 2013], a CO₂ concentration of 2400 ppmv (which represents approximately three doublings from the preindustrial CO₂ level of 280 ppmv) would produce about 9°C of warming on the modern Earth—almost the amount observed during the Cenomanian. Solar luminosity at 100 Ma was about 1% less than at present, though, which is equivalent to half a CO₂ doubling, or a temperature decrease of 1.5°C. So we can account for about 7.5°C of warming out of a desired 10°C. There may indeed be a deficit of CO₂ during the Cenomanian, but if so, it is not that large, and it could be explained in other ways (such as higher climate sensitivity or higher CH₄), without invoking changes in O₂ concentration.

What about the postulated changes in atmospheric O₂? Poulsen *et al.* cite two references on this subject: Falkowski *et al.* [2005] and Tappert *et al.* [2013]. Berner was a coauthor on the Falkowski *et al.* paper, and they have relied on his geochemical cycle model [Berner and Canfield, 1989; Berner *et al.*, 2000] for their predicted Cenomanian O₂ levels. An updated version of Berner's model is described in Berner [2006]. This model is driven by the carbon isotope record in carbonates, which can be used to estimate the rate of burial of organic carbon in sediments. It predicts high atmospheric O₂ (~30%) around 300 Ma, following the deposition of the Carboniferous coal beds and a minimum of O₂ (at ~12%) at the beginning of the Jurassic around 200 Ma. O₂ then increases steadily during the Jurassic and Cretaceous, reaching approximately 18% by the Cenomanian (94–100 Ma). So this model does not offer much support for low O₂ during the period of greatest climatic warmth in the Cenomanian.

Moreover, O₂ models driven by carbon isotopes are poorly conditioned, as small errors in measured ¹³C/¹²C ratios can cause considerable changes to the results. For example, a 1‰ change in δ¹³C (which is small compared to the scatter in the data) corresponds to a change in the organic carbon burial rate of ~2 × 10¹¹ mol/yr. When integrated over 10⁸ years, this corresponds to an O₂ amount of ~2 × 10⁹ mol or about half the O₂ content of the modern atmosphere. This may explain why an alternative model for the evolution of atmospheric O₂ [Bergman *et al.*, 2004], which is also driven by carbon isotopes, predicts 30% O₂ at 100 Ma. Both models are heavily influenced by the uncertainties in the data, as well as the particular form of their C-O cycle parameterization.

The other paleo-O₂ reference cited by Poulsen *et al.* is Tappert *et al.* [2013]. These authors estimate O₂ levels from δ¹³C in plant resins. The carbon isotopic composition of these resins is a complicated function of atmospheric O₂ and CO₂. Higher CO₂ corresponds to lower O₂. When the authors use the (higher) CO₂ levels calculated from models or inferred from pedogenic carbonates, they estimate O₂ concentrations of

explain the warm climate of the middle Cretaceous and early Paleogene, and the second is that O₂ levels were significantly lower in the Cretaceous than they are today.

Consider the CO₂ argument first. Following Bice *et al.* [2006], Poulsen *et al.* cite a median CO₂ concentration of 1120 ppmv for the Cenomanian stage, ~100 million years before present (Ma). But the Bice *et al.* error bars are at least a factor of 2, with a quoted upper limit on CO₂ of 2400 ppmv. Meanwhile, they estimate that tropical sea surface temperatures were at least 5°C warmer than today. Global mean surface temperatures, then, were probably

~11% at 100 Ma (see their Figure 10). So this paper serves as the basis for the low Cenomanian O₂ levels preferred by Poulsen et al. It remains to be determined whether this method of analysis is robust.

As one more reason for skepticism, we also wonder whether an O₂ level as low as 11% would have been enough to support the large, active dinosaurs and early placental mammals that lived during the Cenomanian, both of which have considerable oxygen demands (large terrestrial dinosaurs because of their massive size and energy demands and placental mammals because of their high metabolism and the necessity for high ambient oxygen to effectively facilitate this reproductive strategy) [Falkowski et al., 2005]. From a purely physiological standpoint, it seems that Cenomanian O₂ levels should have been relatively high.

6. Conclusions

In conclusion, the effect of changes in atmospheric O₂ on surface temperature depends on the type of climate model used to study it. Our 1-D, coupled photochemical-climate model predicts a response to changing O₂ levels that is about half as large and opposite in sign from that predicted by the 3-D climate model of Poulsen et al. The climatic response of our model is dominated by pressure broadening of absorption lines of CO₂ and H₂O, which causes the greenhouse effect to increase at higher atmospheric O₂ levels and decrease at lower atmospheric O₂. Changes in Rayleigh scattering push surface temperature in the opposite direction, but this effect is outweighed in our model by the change in pressure broadening. The Poulsen et al. results appear to be largely driven by cloud feedbacks and should thus be checked with one or more independent 3-D climate models before their interpretation of O₂ as a climate driver is accepted. Given the large uncertainties in past levels of both O₂ and CO₂, we agree with Berner [2006] that Phanerozoic climate has been driven largely by changes in atmospheric CO₂ and solar luminosity, coupled with changes in continental geography.

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References

- Bergman, N. M., T. M. Lenton, and A. J. Watson (2004), COPSE: A new model of biogeochemical cycling over Phanerozoic time, *Am. J. Sci.*, **304**, 397–437.
- Berner, R. A. (2006), GEOCARBSULF: A combined model for Phanerozoic atmospheric O₂ and CO₂, *Geochim. Cosmochim. Acta*, **70**, 5653–5664.
- Berner, R. A., and D. E. Canfield (1989), A new model for atmospheric oxygen over Phanerozoic time, *Am. J. Sci.*, **289**, 333–361.
- Berner, R. A., et al. (2000), Isotope fractionation and atmospheric oxygen: Implications for Phanerozoic O₂ evolution, *Science*, **287**, 1630–1633.
- Bice, K. L., D. Birgel, P. A. Meyers, K. A. Dahl, K.-U. Hinrichs, and R. D. Norris (2006), A multiple proxy and model study of Cretaceous upper ocean temperatures and atmospheric CO₂ concentrations, *Paleoceanography*, **21**, PA2002, doi:10.1029/2005PA001203.
- Falkowski, P. G., M. E. Katz, A. J. Milligan, K. Fennel, B. S. Cramer, M. P. Aubry, R. A. Berner, M. J. Novacek, and W. M. Zapol (2005), The rise of oxygen over the past 205 million years and the evolution of large placental mammals, *Science*, **309**, 2202–2204.
- Friedrich, O., R. D. Norris, and J. Erbacher (2012), Evolution of middle to Late Cretaceous oceans—A 55 m.y. record of Earth's temperature and carbon cycle, *Geology*, **40**, 107–110.
- Goldblatt, C. (2016), Comment on: Long-term climate forcing by atmospheric oxygen concentrations, *Science*, **353**, 132.
- Goldblatt, C., A. J. Matthews, M. W. Claire, T. M. Lenton, A. J. Watson, and K. J. Zahnle (2009), Nitrogen-enhanced greenhouse warming on early Earth, *Nat. Geosci.*, **2**(12), 891–896.
- Intergovernmental Panel on Climate Change (2013), *Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*, edited by T. F. Stocker et al., pp. 1535, Cambridge Univ. Press, Cambridge, U. K.
- Kiehl, J. T., J. J. Hack, and J. W. Hurrell (1998), The energy budget of the NCAR Community Climate Model: CCM3, *J. Clim.*, **11**, 1151–1178.
- Manabe, S., and R. T. Wetherald (1967), Thermal equilibrium of the atmosphere with a given distribution of relative humidity, *J. Atmos. Sci.*, **24**, 241–259.
- Mlawer, E. J., S. J. Taubman, P. D. Brown, M. J. Iacono, and S. A. Clough (1997), Radiative transfer for inhomogeneous atmospheres: RRTM, a validated correlated-k model of the longwave, *J. Geophys. Res.*, **102**, 16,663–16,682, doi:10.1029/97JD00237.
- Poulsen, C. J., C. R. Tabor, and J. D. White (2015), Long-term climate forcing by atmospheric oxygen concentrations, *Science*, **348**, 1238–1241.
- Scott, A. C., and I. J. Glasspool (2006), The diversification of Paleozoic fire systems and fluctuations in atmospheric oxygen concentration, *Proc. Natl. Acad. Sci. U.S.A.*, **103**(29), 10,861–10,865.
- Segura, A., K. Krelow, J. F. Kasting, D. Sommerlatt, V. Meadows, D. Crisp, M. Cohen, and E. Mlawer (2003), Ozone concentrations and ultraviolet fluxes on Earth-like planets around other stars, *Astrobiology*, **3**, 689–708.
- Strong, J., and G. N. Plass (1950), The effect of pressure broadening of spectral lines on atmospheric temperature, *Astrophys. J.*, **112**, 365–379.
- Tappert, R., R. C. McKellar, A. P. Wolfe, M. C. Tappert, J. Ortega-Blanco, and K. Muehlenbachs (2013), Stable carbon isotopes of C3 plant resins and ambers record changes in atmospheric oxygen since the Triassic, *Geochim. Cosmochim. Acta*, **121**, 240–262.